

# PATENT SPECIFICATION

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## (54) PAPER TREATMENT PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the removal of printing ink from printed paper, and more particularly to a two-stage process combining non-aqueous and aqueous treatments.

15 It has long been known to repulp printed paper, particularly newsprint, and to reconvert this pulp into fresh paper. However, unless the printing ink is first removed from such printed paper, the fresh paper made from it will be coloured by the ink and suitable for low grade uses only. It is therefore desirable that printed paper which is to be reprocessed should first be de-inked as thoroughly as possible.

25 De-inking has been carried out by aqueous processes in which the printed paper is cooked and pulped in the presence of alkali, surface-active agents and bleaches such as hypochlorite or sodium peroxide. In another process the waste paper is pulped with aqueous alkali and soap, calcium salts are added and air is blown through the pulp, when the ink particles come to the surface as a froth, which is removed by suitable means. De-inking may also be achieved by treatment of the paper with a solution of a surface-active agent in a non-aqueous solvent.

40 According to the present invention there is provided a process for the removal of printing ink from printed paper which comprises impregnating the paper with an oil-soluble, substantially water-insoluble surface-active agent, pulping and thereby de-inking the impregnated paper in an aqueous alkaline medium and separating the de-inked pulp from the aqueous alkaline medium.

45 The process is particularly applicable to paper derived from wood pulp cellulose, such

as newsprint, but may also be used for the de-inking of paper containing, or consisting of, other fibres, for example, esparto, cotton, bagasse, straw, linen, bamboo, sisal or jute.

The paper may also contain any of those fillers and other adjuvants which are conventionally added during the paper-making process. In addition to black, carbon-based inks, the process is also effective in removing from paper those inks derived from coloured pigments, both organic and inorganic.

The inks used for printing newsprint are based on non-drying oils as the pigment vehicle. Examples of such oils are petroleum oil, mineral oil, spindle oil and lubricating oil. Letterpress inks employ heat-bodied linseed or other drying oils as the pigment vehicle and may also contain hard resins and long oil alkyds, while inks for gravure printing may contain zinc and calcium rosins, cyclised rubber and Alloprene (Registered Trade Mark). The present process is applicable to the removal of any of these inks, but is particularly effective in the case of inks based on non-drying oils.

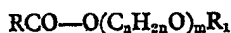
As examples of the surface-active agents which are suitable for use in the present process there may be mentioned the following classes:

1. The condensation products of from 1.5 to 6.0 molecular proportions of ethylene oxide with 1 molecular proportion of an aliphatic alcohol or mixture of aliphatic alcohols containing from 11 to 20 carbon atoms. Examples of such alcohols are cetyl, oleyl, lauryl, myristyl and stearyl alcohols. Preferred agents within this class are those in which from 2.0 to 4.0 molecular proportions of ethylene oxide are condensed with 1 molecular proportion of the aliphatic alcohol or mixture of alcohols as defined above. Particularly preferred is the condensation product of 3.5 molecular proportions of ethylene oxide with 1 molecular proportion of a mixture of cetyl alcohol and oleyl alcohol, this mixture being commercially available under the name spermanol.

2. The surface-active agents which are derived from a polyol by, in either order, at

R.CO represents the acyl radical of a

3. The surface active agents having the general formula:



5 wherein RCO— represents the acyl radical of an unsaturated or branched chain fatty acid containing from 12 to 22 carbon atoms;

R<sub>1</sub> represents an alkyl or alkenyl radical containing from 1 to 4 carbon atoms;

10 n is an integer from 2 to 4 and

m is an integer from 2 to 20

As examples of unsaturated acyl radicals represented by RCO— there may be mentioned the radicals derived from oleic acid, 15 linoleic acid, linolenic acid and commercial mixtures of these acids such as soya bean fatty acids, linseed fatty acids and tall oil fatty acids which may also contain minor proportions of saturated fatty acids and/or rosin acids.

As examples of branched chain acyl radicals represented by RCO— there may be mentioned the radicals derived from the commercial synthetic acids obtained by oxidation of petroleum stocks and paraffin waxes.

As examples of alkyl and alkenyl radicals represented by R<sub>1</sub> there may be mentioned methyl, ethyl, propyl, isopropyl, butyl, isobutyl, butenyl and propargyl, but it is preferred that R<sub>1</sub> represents a methyl radical or an ethyl radical.

It is also preferred that the integer n is 2 or 3 and that the integer m has a value of from 3 to 8.

35 The oxyalkylene units in the polyoxyalkylene chain represented by (C<sub>n</sub>H<sub>2n</sub>O)<sub>m</sub> in the above formula need not all be the same, and when they are different the polyoxyalkylene chain may be in the form of a random copolymer or a block copolymer.

40 The surface-active agents having the above general formula may be obtained by esterification or transesterification reactions between acids of the formula RCOOH or their derivatives and alkylene oxide condensates having the formula R<sub>1</sub>O(C<sub>n</sub>H<sub>2n</sub>O)<sub>m</sub>H wherein R, R<sub>1</sub>, n and m have the meanings defined above. These latter intermediates are themselves obtained by the condensation of an alcohol or phenol R<sub>1</sub>OH, wherein R<sub>1</sub> has the meaning defined above, with one or more alkylene oxides. Mixtures of alcohol may be used.

4. The surface-active agents having the general formula:



55 wherein RCO— represents the acyl radical of an unsaturated or branched chain fatty acid containing from 10 to 22 carbon atoms;

60 R<sub>1</sub> represents an alkyl or alkenyl radical containing from 10 to 22 carbon atoms

or a phenyl, naphthyl, alkylphenyl, alkylnaphthyl, arylphenyl, aralkylphenyl, alkarylphenyl or aralkyl radical.

n is an integer from 2 to 4, and

m is an integer from 2 to 30

As examples of unsaturated acyl radicals represented by RCO— there may be mentioned the radicals derived from oleic acid, linoleic acid, linolenic acid and commercial mixtures of these acids such as soya bean fatty acids, linseed fatty acids, and tall oil fatty acids, which may also contain minor proportions of saturated fatty acids and/or rosin acids.

As examples of branched chain acyl radicals represented by RCO— there may be mentioned the radicals derived from the commercial synthetic acids obtained by oxidation of petroleum stocks and paraffin waxes.

As examples of the radicals represented by R<sub>1</sub> there may be mentioned dodecyl, cetyl, octadecyl, oleyl, the radicals of the branched chain C<sub>12</sub>—C<sub>18</sub> alcohols obtained by carbonylation of olefins or by oxidation of paraffin hydrocarbons, benzyl, diisopropyl - β - naphthyl, straight or branched chain nonyl phenyl, o- or p-benzylphenyl and o- or p-phenylphenyl.

It is preferred that the integer n is 2 or 3 and that the integer m has a value of from 6 to 18 when R<sub>1</sub> is an alkyl or alkenyl radical and from 6 to 16 when R<sub>1</sub> is an aromatic group-containing radical.

The oxyalkylene units in the polyoxyalkylene chain represented by (C<sub>n</sub>H<sub>2n</sub>O)<sub>m</sub> in the above formula need not all be the same, and when they are different the polyoxyalkylene chain may be in the form of a random copolymer or a block copolymer.

The surface-active agents having the above general formula may be obtained by esterification or transesterification reactions between acids of the formula RCOOH or their derivatives and alkylene oxide condensates of the formula R<sub>1</sub>O(C<sub>n</sub>H<sub>2n</sub>O)<sub>m</sub>H wherein R, R<sub>1</sub>, n and m have the meanings defined above. These latter intermediates are themselves obtained by the condensation of an alcohol or phenol R<sub>1</sub>OH, wherein R<sub>1</sub> has the meaning defined above, with one or more alkylene oxides. Mixtures of alcohols or phenols R<sub>1</sub>OH may be used, for example, the commercial cetyl/oleyl alcohol mixtures obtained from sperm oil.

The above-defined classes of surface-active agents are all soluble in the oily vehicles which form the basis of most printing inks, but are substantially insoluble in water.

The surface-active agents which may be used in the process are not confined to the above classes, and any oil-soluble, substantially water-insoluble agent will normally be effective. Mixtures of agents may be used.

The surface-active agent is most conveniently applied to the printed paper which is to

be de-inked as a solution in a water-insoluble solvent, for example, hydrocarbon solvents such as toluene, solvent naphtha, white spirit, xylene and cyclohexane, and chlorinated hydrocarbon solvents such as perchloroethylene, trichloroethylene, methylene chloride and tetrachlorethane, a preferred solvent being kerosene.

The solvent may be of high volatility, so that after the solution of surface-active agent has been applied to the paper the solvent evaporates rapidly, leaving the paper impregnated with surface-active agent alone.

In this case it is desirable to provide means for collecting and condensing the vapours of such volatile solvents to prevent loss of solvent and to minimise the concentration of the solvent in the atmosphere. However, it is preferred to use a solvent having a boiling point above 100°C., so that the paper being treated remains impregnated with both solvent and surface-active agent.

The paper to be treated is impregnated with the surface-active agent, or solution of the surface-active agent by any suitable means, and the excess agent or solution is preferably removed, for example, by filtration, pressing or centrifugal means, before the paper is further treated in an aqueous alkaline medium. The paper is preferably shredded or otherwise converted into relatively small pieces before treatment, and should also be free from dirt and other extraneous matter.

After the paper has been impregnated with surface-active agent, or surface-active agent and solvent, the de-inking is accomplished by treating the impregnated paper in an aqueous alkaline medium. The treatment is conveniently carried out in the conventional beating-equipment used in paper-making. The aqueous alkaline medium is a solution in water of an alkaline agent, for example, sodium silicate, sodium hydroxide, sodium carbonate, sodium sesquicarbonate, trisodium phosphate, sodium pyrophosphate, sodium polyphosphate, sodium aluminate and sodium acetate. The corresponding potassium compounds may also be used. The concentration of alkaline agent in the aqueous solution may be up to 10% by weight, and is preferably in the range 0.5% to 5% by weight. The aqueous alkaline treatment will normally be carried out at room temperature, although higher temperatures may be used if desired, and is continued until the paper is fully disintegrated. Treatment times in the region of 30 minutes are usually sufficient.

The pulp so-obtained is then collected on a wire mesh sieve or other suitable filter, when the aqueous liquor containing the suspended ink passes through, leaving the de-inked pulp on the filter. The treated pulp is then preferably washed at least once by re-slurrying in water and repeating the filtration process. The

pulp may then be re-converted into paper by conventional means. In the case of printed newsprint the paper which is re-made after de-inking by the process of the present invention is generally at least equal in appearance to the original unprinted paper, and may even be of a superior degree of whiteness, without the use of any bleaching treatment. However, a bleach treatment may be incorporated during the de-inking stage of the process, and is particularly useful when all or part of the paper being treated has been dyed or tinted.

In a modification of the process, the printed paper is pulped in an emulsion of the surface-active agent, or surface-active agent and solvent, in the aqueous alkaline medium, the de-inked pulp then being filtered off and washed as described above.

The invention is illustrated but not limited by the following Examples in which parts and percentages are by weight, unless otherwise stated, the relationship between the parts by weight and parts by volume being that of the kilogram to the litre.

#### Example 1

2.5 parts of dry, printed newsprint are soaked in 100 parts by volume of a 5% v/v solution in kerosene of a condensate of 3.5 molecular proportions of ethylene oxide with 1 molecular proportion of a mixture of cetyl alcohol and oleyl alcohol. The excess solution is squeezed out of the soaked paper, which is then beaten for 10 minutes in 100 parts by volume of a 5% w/v solution of sodium silicate in water. The resulting pulp is filtered on a 60 mesh sieve and washed twice by a re-slurrying with 200 parts by volume of cold water. A hand sheet made from the final pulp is essentially free from printing ink. The condensate of ethylene oxide with mixed cetyl/oleyl alcohols which is used in this Example may be replaced by an equal amount of a condensate of from 3 to 9 molecular proportions of ethylene oxide with 1 molecular proportion of tall oil fatty acids without loss of de-inking efficiency.

#### Example 2

3 parts by volume of the kerosene solution of a cetyl/oleyl alcohol-ethylene oxide condensate employed in Example 1 is emulsified in 100 parts by volume of a 5% w/w aqueous solution of sodium silicate using a high speed mixer. 2.5 parts of dry, printed newsprint are beaten into this emulsion for 10 minutes. The resulting pulp is then filtered and washed as described in Example 1. A hand sheet made from the pulp is essentially free from printing ink. The condensate of ethylene oxide with mixed cetyl-oleyl alcohols which is used in this Example may be replaced by an equal amount of a condensate of from 3 to 9 molecular proportions of ethylene oxide with 1



- acid containing from 12 to 22 carbon atoms;
- $R_1$  represents an alkyl or alkenyl radical containing from 1 to 4 carbon atoms;
- 5  $n$  is an integer from 2 to 4 and  $m$  is an integer from 2 to 20.
17. A process as claimed in claim 16 wherein  $R_1$  in the general formula represents a methyl radical or an ethyl radical.
- 10 18. A process as claimed in claim 16 or claim 17 wherein in the general formula  $n$  is 2 or 3 and  $m$  has a value from 3 to 8.
- 15 19. A process as claimed in any one of claims 16 to 18 wherein, in the polyoxyalkylene chain represented by  $C_nH_{2n}O$  in the general formula, the values of  $n$  are not all the same.
- 20 20. A process as claimed in claim 19 wherein the polyoxyalkylene chain is in the form of a random copolymer.
21. A process as claimed in claim 19 wherein the polyoxyalkylene chain is in the form of a block copolymer.
- 25 22. A process as claimed in claim 1 wherein the surface-active agent has the general formula:
- $$RCO-O(C_nH_{2n}O)_mR_1$$
- wherein  $RCO-$  represents the acyl radical of an unsaturated or branched chain fatty acid containing from 10 to 22 carbon atoms;
- 30  $R_1$  represents an alkyl or alkenyl radical containing from 10 to 22 carbon atoms or a phenyl, naphthyl, alkylphenyl, alkyl-naphthyl, arylphenyl, aralkylphenyl, alkarylphenyl or aralkyl radical,
- 35  $n$  is an integer from 2 to 4, and  $m$  is an integer from 2 to 30.
- 40 23. A process as claimed in claim 22 wherein, in the general formula,  $n$  is 2 or 3 and  $m$  has a value of from 6 to 18 when  $R_1$  is an alkyl or alkenyl radical and from 6 to 16 when  $R_1$  is an aromatic group-containing radical.
- 45 24. A process as claimed in claim 22 wherein the polyoxyalkylene chain represented by  $C_nH_{2n}O$  in the general formula, the values of  $n$  are not all the same.
- 50 25. A process as claimed in claim 24 wherein the polyoxyalkylene chain is in the form of a random copolymer.
26. A process as claimed in claim 24 wherein the polyoxyalkylene chain is in the form of a block copolymer.
- 55 27. A process as claimed in any one of claims 1 to 26 wherein the surface-active agent is employed as a solution in a water-insoluble solvent.
28. A process as claimed in claim 27 wherein the water-insoluble solvent has a boiling point above  $100^\circ\text{C}$ .
- 60 29. A process as claimed in claim 27 or claim 28 wherein the water-insoluble solvent is kerosene.
30. A process as claimed in any one of claims 1 to 29 wherein the paper is shredded or otherwise converted into relatively small pieces before treatment.
- 65 31. A process as claimed in any one of claims 1 to 30 wherein the concentration of alkaline agent in the aqueous alkaline medium is from 0.5 to 5.0% by weight.
- 70 32. A process as claimed in any one of claims 1 to 31 which is carried out at room temperature.
- 75 33. A process as claimed in any one of claims 1 to 32 wherein a bleach treatment is incorporated during the de-inking stage.
34. A modification of the process claimed in any one of claims 1 to 33 wherein the printed paper is pulped in an emulsion of the surface-active agent, or surface-active agent and water-insoluble solvent, in the aqueous alkaline medium, followed by separation of the de-inked pulp from the aqueous alkaline medium.
- 80 35. A process as claimed in any one of claims 1 to 34 wherein the de-inked pulp is washed at least once by re-slurrying in water followed by separation of the pulp from the wash water.
- 85 36. A process for the removal of printing ink from printed paper substantially as hereinbefore described, especially with reference to the foregoing Examples.
- 90 37. De-inked paper pulp, substantially as hereinbefore described, especially with reference to the foregoing Examples.
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Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act 1949, to patent No. 1,004,466.